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Influence of the Bridging Atom on the Performance of a Low-Bandgap Bulk Heterojunction Solar Cell

By Markus C. Scharber,* Markus Koppe, Jia Gao, Fabrizio Cordella, Maria. A. Loi, Patrick Denk, Mauro Morana, Hans-Joachim Egelhaaf, Karen Forberich, Gilles Dennler, Russ Gaudiana, Dave Waller, Zhengguo Zhu, Xiaobo Shi, and Christoph J. Brabec

Bulk heterojunction solar cells have attracted considerable attention over the past several years due to their potential for low-cost photovoltaic technology. The possibility of manufacturing modules via a standard printing/coating method in a roll-to-roll process in combination with the use of low-cost materials will lead to a watt-peak price of less than 1 US\$ within the next few years.^[1]

Despite the low-cost potential, the power conversion efficiency of bulk heterojunction devices is low compared to inorganic solar cells. Efficiencies in the range of 5–6% have been certified at NREL and AIST usually on devices with small active areas.^[2]

The current understanding of bulk heterojunction solar cells suggests that the maximum efficiency is in the range of 10–12%.^[3] Several reasons for the power conversion efficiency limitation have been identified.^[1] Some of the prerequisites for achieving highest efficiencies are donor and acceptor materials with optimized energy levels [highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)], efficient charge transport in the donor–acceptor blend, efficient charge generation and limited recombination losses. Power conversion efficiency is strongly dependent on charge transport and charge generation, which are dominated by the phase behavior of the donor and acceptor molecules. The resulting, and often unfavorable, nanomorphology of this two-component blend limits the power conversion efficiency of bulk heterojunction solar cells. Precise control of the nanomorphology is very difficult and has been achieved only for a few systems.^[4–6] The relation between the chemical structure of donor and acceptor materials and the nanomorphology that they form when they are blended is currently not well understood, and as will be shown in this paper, minor changes in the chemical structure can cause major changes in the performance of the materials in organic solar cells.

In this work we demonstrate the effect of replacing a carbon atom with a silicon atom on the main chain of the conjugated polymer. The approach has been used previously, and promising materials for field-effect transistors and organic solar cells have been demonstrated.^[7–9] We find that making this simple substitution in poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) yields a polysilole, e.g., poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d']silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl] (Si-PCPDTBT), with a higher crystallinity, improved charge transport properties, reduced bimolecular recombination, and a reduced formation of charge transfer complexes when blended with a fullerene derivative. This silole-based polymer is found to form a highly functional nanomorphology when blended with [6,6]-phenyl C71-butyric acid methyl ester (C₇₀-PCBM), and solar cells prepared using this blend gave efficiencies of 5.2%, certified by the National Renewable Energy Laboratory.^[11] The presented polymer is the first low-bandgap semiconducting polymer to have a certified efficiency of over 5%.

The chemical structure of the subject polymer is shown in Figure 1. The material was synthesized following the procedure described previously.^[10] The synthesis and properties of the carbon-bridged polymer have been described before.^[11,12] Figure 2a shows the absorbance and photoluminescence (PL) spectra of a thin solid film of the pristine Si-bridged polymer and a blend with [6,6]-phenyl C61-butyric acid methyl ester (PCBM) (1:1 wt %). In the absorbance spectrum, a strong aggregation feature is present in the range between 600 and 800 nm, indicating that the polymer chains tend to stack even in the presence of PCBM. This is confirmed by grazing incidence X-ray studies (Fig. 1b), which show a pronounced feature at 5.2° (17 Å), which is typical for hexyl groups separating the main chains, and a weak reflection at around 20° corresponding to the π – π stacking (4 Å).^[13] In contrast, the carbon-bridged polymer is more amorphous, as indicated by the broad featureless absorption (Fig. 2b) and grazing incidence X-ray studies (Fig. 1b).^[12] The strong stacking of the Si-bridged material leads to limited solubility of the polymer in common organic solvents, and with higher molecular weight materials (number average molecular weight, $M_n > 25$ kDa; weight-average molecular weight $M_w > 40$ kDa), the polymers can only be processed at elevated temperatures.

The PL spectra of the pristine Si-bridged polymer and a blend of the same material with PCBM are shown in Figure 2a. By adding PCBM (1:1 wt%), the PL is quenched by a factor of ~50, but the spectrum retains its spectral feature around 900 nm. From

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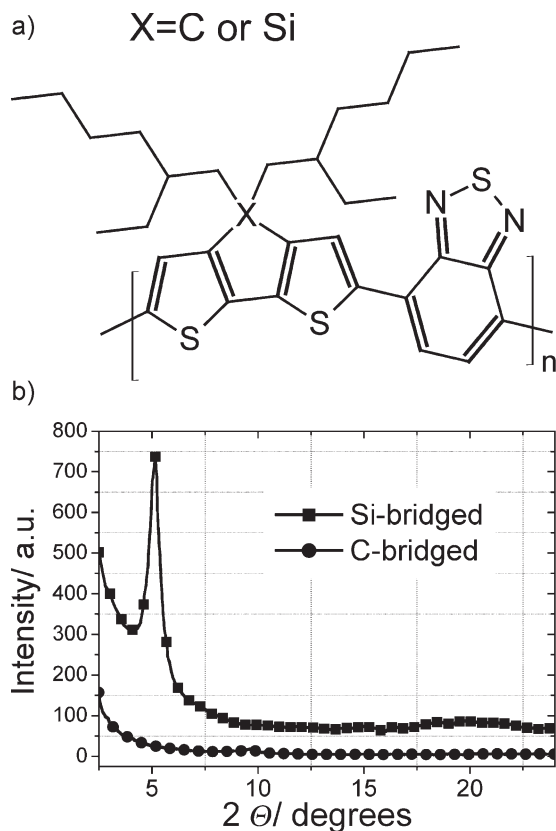


Figure 1. a) Chemical structure of the polymer, poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-b-(2,1,3-benzothiadiazole))] for X = carbon, poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole-2-thienyl)-2,1,3-benzothiadiazole-5,5'-diyl] for X = silicon. b) Diffractometry images of films of pristine silicon-bridged (squares) and carbon bridged polymer deposited on quartz substrates.

transient measurements we extracted the exciton lifetime of the Si-bridged polymer. A monoexponential decay with a time constant of about 65 ps was found for the pristine polymer. For comparison in poly-3-hexylthiophene, one of the standard p-type semiconductors used in organic solar cells, a PL decay lifetime of 640 ps was observed.^[14] The short exciton lifetime explains the low PL quantum yield of the polymer. Fast excitation decay could also lead to limitations in charge-generation efficiency in blends with PCBM especially when the polymer domains are too large to allow efficient exciton diffusion to the charge separating donor-acceptor interface. However, it does not seem to be the case because the decay of the PL in the blend is limited by the experimental setup (~5 ps).

Figure 2b shows the PL of the carbon-bridged polymer and a blend of the same material with PCBM. The exciton lifetime in the pristine carbon-bridged polymer was found to be only ~45 ps. Again adding PCBM causes a quenching of the polymer PL. In addition, the PL-spectrum is red-shifted and shows a long-living component. This makes a detailed analysis of the PL-decay difficult and we were not able to determine the PL-quenching precisely. A rough estimation taking into consideration continuous wave (cw)-PL measurements gives a quenching factor ≥ 10 for the exciton emission of the polymer in the presence of PCBM.

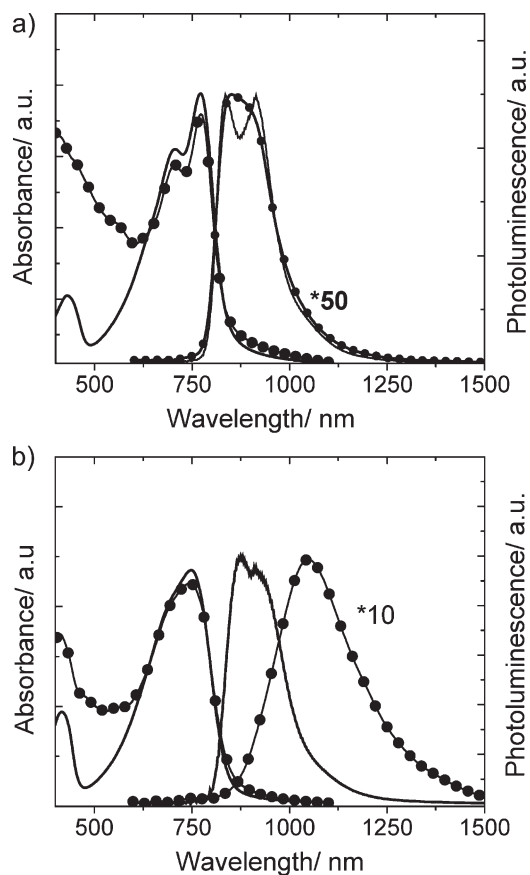


Figure 2. a) Si-PCPD TBT; b) PCPD TBT; normalized absorbance and PL of the pristine polymer (line) and a polymer:fullerene blend (1:1 wt ratio) (line + circles) films ($d = 100$ nm), $\lambda_{\text{exc}} = 780$ nm.

The observed long-lived component indicates that a charge-transfer state^[15–17] is active in this system, which can have detrimental consequences for the solar-cell performance.^[17]

Cyclic voltammetry was conducted to determine the HOMO and LUMO level of the silole-based polymer. The measurements were performed on thin films. The HOMO and LUMO-levels were determined from the onset of the oxidation and reduction current and we found -5.3 and -3.6 eV for the HOMO and LUMO level, respectively [vs. the normal hydrogen electrode (NHE) standard (-4.75 eV)]. These values are comparable to those found for the C-bridged polymer and would suggest that power conversion efficiencies in the range of 6–7% are achievable when blended PCBM.^[3]

In Table 1 the charge-carrier mobilities found in C- and the Si-bridged polymers and their blends with C₇₀-PCBM (1:2 wt%) are summarized. Mobilities were extracted from field-effect transistor characteristics using the same device layout and fabrication method for all measurements. A detailed description of the transistor characteristic analysis procedure and the effect of charge carrier density and device layout can be found in Morana et al.^[18]

For pristine films the hole mobilities of PCPD TBT and Si-PCPD TBT were found to differ by a factor of 2, with the Si-bridged polymer having the higher mobility. A molecular weight M_n larger than 20 kDa was necessary to achieve the

Table 1. OFET mobility

	Pristine polymer	Blend with C70-PCBM (1:2)	
	μ_h [$\text{cm}^2 \text{Vs}^{-1}$]	μ_h [$\text{cm}^2 \text{Vs}^{-1}$]	μ_e [$\text{cm}^2 \text{Vs}^{-1}$]
C-bridged [12]	5×10^{-3}	3×10^{-4}	4×10^{-4}
Si-bridged	1×10^{-2}	1×10^{-3}	1×10^{-3}

mobilities listed in Table 1. Balanced electron and hole mobilities could be obtained by blending the polymers with C₇₀-PCBM (weight ratio 1:2). Electron and hole mobilities were found to be about a factor of 2–3 lower in the blend with the carbon-bridged material compared to the blend with the silicon-bridged polymer. Overall, the mobilities for the Si-bridged polymer exceed those of the C-bridged polymer by 2–3 in all investigated cases.

In Figure 3a the current–voltage curves (dark and under AM1.5 illumination) of Si-bridged/C₇₀-PCBM devices are shown. The same device was certified at NREL at an efficiency of 5.24% (open-circuit voltage, $V_{oc} = 0.576$ V, short-circuit current density, $J_{sc} = 14.92 \text{ mA cm}^{-2}$, fill factor, FF = 61%),^[1] which is in very good agreement with the efficiency measured in our laboratory. These high-performance solar cells have an active layer thickness in the range of 100–140 nm. By increasing the layer thickness, short-circuit current densities of up to 17 mA cm^{-2} could be achieved. However, these devices exhibited a slightly lower V_{oc}

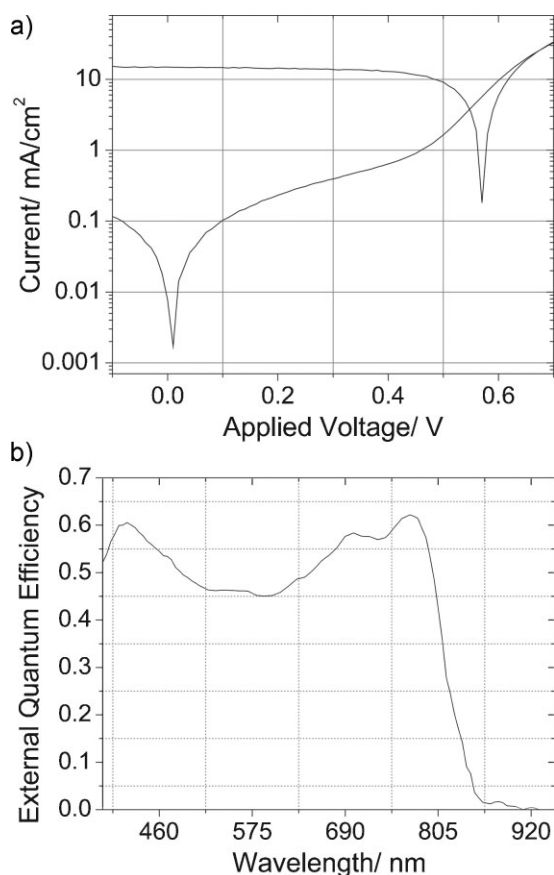


Figure 3. a) Current–voltage curves, $V_{oc} = 0.57$ V, FF = 0.62, $J_{sc} = 14.9 \text{ mA cm}^{-2}$ measured under 100 mW cm^{-2} AM1.5G; b) EQE the 0.753 cm^2 device.

and a significantly lower FF resulting in overall efficiencies below 5%. Devices prepared using the carbon-bridged polymer show a power conversion efficiency around 3% with a maximum external quantum efficiency (EQE) of 35%^[11] and only the addition of octanedithiol allowed the preparation of solar cells with an EQE of ~50% at 800 nm.^[6]

Figure 3b shows the EQE of the investigated device. EQE reaches a maximum value of 62% at 770 nm. The EQE spectrum shows an onset at around 900 nm with a steep increase starting at 860 nm. By increasing the active layer thickness, the EQE shows an almost rectangular shape and saturates around 65%. Applying an additional white light bias equivalent to 1 sun, the EQE of a typical device decreases by 1–2% (relative) compared to the EQE measured under monochromatic low light conditions. This indicates that bimolecular recombination is active but rather weak under short circuit conditions in the device. By applying a reverse bias voltage up to -1.5 V to the solar cell in addition to the white light bias, the EQE of Si-bridged devices gradually increases by about 3–4% (relative). The observed weak electric field dependence of the EQE shows that a dominant fraction of the photogenerated charge carriers can be extracted under short-circuit conditions. An increase in the electric field, which extracts charge carriers, may partially reduce the bimolecular recombination but does not significantly enhance the formation of free charge carriers. The internal quantum efficiency of the certified device was estimated by optical modeling.^[19] Best fits resulted in an IQE of 75–80% over the whole spectrum. Since the investigated layer stack may have some inhomogeneities, the layers may have an intrinsic roughness which is not considered in our model and the optical constants available for the materials have some uncertainties, the calculated IQE may only be a lower limit for the absorbed photon to electron conversion efficiency of our device.

We also estimated the bimolecular recombination coefficient β for optimized carbon- and silicon-based polymer-fullerene devices by transient photo-voltage spectroscopy.^[20] The Langevin recombination^[21] coefficient β_L is given by $e(\mu_e + \mu_h)/(\epsilon\epsilon_0)$ where e is the electronic charge, ϵ and ϵ_0 are the relative and absolute dielectric permittivity and μ_e and μ_h are the electron and hole mobility. Langevin-type recombination^[20] was found for carbon-bridged solar cells ($\beta_L \sim \beta = 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$). The Si-bridged devices exhibit a non-Langevin-type recombination with a $\sim 200 \times$ reduction for the recombination coefficient ($\beta = 5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$) compared to the calculated Langevin coefficient ($\beta_L = 1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$). β_L was determined using the mobilities shown in Table 1 and $\epsilon = 3$. Our findings support the idea^[21,22] that the bimolecular recombination process can be suppressed by optimizing the nanomorphology of a polymer/fullerene blend.

Replacing the carbon by a silicon atom introduces a small distortion of the cyclopentadithiophene unit. The longer Si–C bond^[23] modifies the geometry of the fused dithiophene unit (Fig. 4) which is enough to achieve a better ordering of the polymer chains leading to above described improvements. Enhanced aggregation of the semiconducting polymer, which may be accompanied by the formation of PCBM clusters, reduces the formation of charge-transfer complexes^[17] and increases the formation of free charge carriers. This seemingly small change from carbon to silicon with the concomitant modification in geometry leading to pronounced structural and electronic

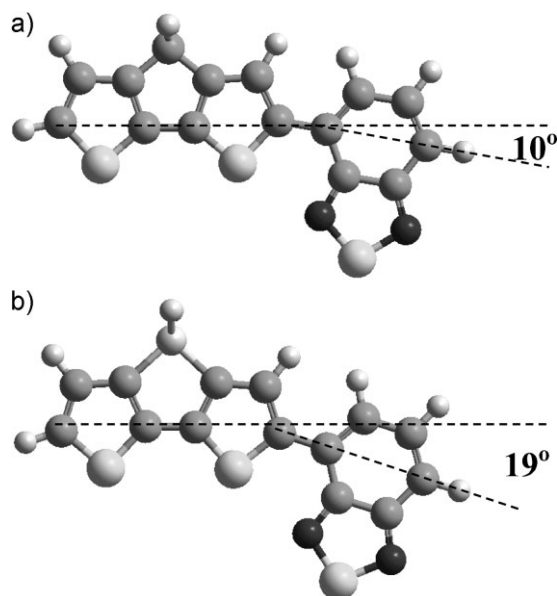


Figure 4. Comparison of the C-bridged a) and Si-bridged b) repeat unit optimized using the AM1 method.

changes and performance illustrates the importance of a careful material design.

In summary, we have compared the electrical and optical properties of PCPDT-BT and Si-PCPDT-BT polymers and their blends with PCBM. Replacing the bridging carbon atom in the cyclopentadithiophene by a silicon atom leads to a more crystalline material that shows no evidence of the formation of a long-lived charge-transfer complex when blended with PCBM. The higher crystallinity of the material when blended with PCBM leads to better charge transport and may also be responsible for the reduced bimolecular recombination. Overall the improved material properties allow the preparation of an efficient low-bandgap organic solar cell which could also be used as the low energy absorber in an organic multijunction device. The study demonstrates the importance of the nanomorphology for good charge generation and transport and suggests that small structural variation can lead to improved material properties and efficient organic solar cells.

Experimental

The preparation of the polymer poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d']silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl] Si-PCPDTBT has been described previously. [10]. Cyclic voltammetry measurements were performed following the procedure described in Mühlbacher et al. [11]. The films used for X-ray diffraction (XRD) measurements were drop-cast on quartz plates cleaved at an angle that would give the smallest signal in the XRD. Measurements were performed in grazing incidence mode. The radiation used was a monochromatic Cu K α beam with a wavelength of $\lambda = 0.154$ nm. For absorbance on PL measurements thin films were cast from solution on a microscope slide. Absorbance measurements were performed on a Perkin Elmer 35 UV-vis spectrometer. For PL measurements all the samples were excited by a 150 fs pulsed Kerr mode locked Ti-sapphire laser at 760 nm or frequency

doubled at 380 nm. The steady PL emission of the samples was measured with an Andor iDus InGaAs detector array. Typical excitation power densities were ~ 5.6 W cm $^{-2}$. The time-resolved PL was recorded by Hamamatsu streak camera working in synchro-scan mode. All the measurements were performed at room temperature under vacuum. Mobility measurements were performed following the procedure described in Morana et al [12]. Devices were prepared as described in the ref. [24]. EQEs were measured by using lock-in amplifier (SR830, Stanford Research Systems) with current preamplifier (HMS-74) under short circuit condition. The devices were illuminated by monochromatic light from a xenon lamp passing through a monochromator (Oriol Conerstone) with a typical intensity of a few μ W. Between the Xenon lamp and the monochromator a mechanical chopper is mounted. Typically chopping frequencies in the range of 10–200 Hz are applied. A calibrated silicon diode (Hamamatsu S2281) is used as a reference.

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